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An agency of Industry Canada

CA 2063877 C 2003/05/13

(11)(21) 2 063 877

(12) BREVET CANADIEN
CANADIAN PATENT

(13) C

(22) Date de dépôt/Filing Date: 1992/03/24

(41) Mise à la disp. pub./Open to Public Insp.: 1992/09/29

(45) Date de délivrance/Issue Date: 2003/05/13

(30) Priorité/Priority: 1991/03/28 (MI91 A 000858) IT

(51) Cl.Int.^{5}/Int.Cl.^{5} E21B 33/138

(72) Inventeurs/Inventors:
LOCKHART, THOMAS PAUL, IT;
ALBONICO, PAOLA, IT

(73) Propriétaires/Owners:
ENIRICERCHE S.P.A., IT;
AGIP S.P.A., IT

(74) Agent: ROBIC

(54) Titre : COMPOSITION AQUEUSE GELIFIABLE A GELIFICATION DIFFEREE

(54) Title: AQUEOUS GELLABLE COMPOSITION WITH DELAYED GELLING TIME

(57) Abrégé/Abstract:
An aqueous gellable composition for use to modify the permeability of high-permeability regions in petroleum reservoirs, wherein the aqueous gellable composition containing an organic, water-soluble polymer crosslinkable with chrome ion and a crosslinking and gel-retarding system definable by the formula: Cr $(L)_m$.nL' L' being in form not complexed with chrome ion wherein: Cr is a trivalent chrome ion; L is an organic ligand consisting of a monocarboxylate or dicarboxylate ion, optionally bearing one or more amino or hydroxy functional group(s), in form complexed with chrome ion; L' is an organic ligand selected among malonic and ascorbic acids or when L' is salicylic acid, L is selected among: acetate, propionate, butyrate, malonate, succinate, glutarate, adipate, glycolate, lactate, alpha-hydroxybutyrate, ascorbate, tartrate, alpha-aminoacetate (glycine) and alpha-amino-beta-hydroxypropionate (serine), alpha-aminobutyrate, phthalate; in form complexed with chromium ion; m has a value comprised within the range of from 1 to 3, depending on the nature of the ligand L; n has a value comprised within the range of from 0.5 to 100; with the proviso that in the crosslinking and gel-retarding system, the ligand L is different from the ligand L'.

ABSTRACT

An aqueous gellable composition for use to modify the permeability of high-permeability regions in petroleum reservoirs, wherein the aqueous gellable composition containing an organic, water-soluble polymer crosslinkable with chrome ion and a crosslinking and gel-retarding system definable by the formula:

$$Cr(L)_m.nL'$$

L' being in form not complexed with chrome ion

wherein:

Cr is a trivalent chrome ion;

L is an organic ligand consisting of a monocarboxylate or dicarboxylate ion, optionally bearing one or more amino or hydroxy functional group(s), in form complexed with chrome ion;

L' is an organic ligand selected among malonic and ascorbic acids or when L' is salicylic acid, L is selected among: acetate, propionate, butyrate, malonate, succinate, glutarate, adipate, glycolate, lactate, alpha-hydroxybutyrate, ascorbate, tartrate, alpha-aminoacetate (glycine) and alpha-amino-beta-hydroxypropionate (serine), alpha-aminobutyrate, phthalate; in form complexed with chromium ion;

m has a value comprised within the range of from 1 to 3, depending on the nature of the ligand L;

n has a value comprised within the range of from 0.5 to 100;

with the proviso that in the crosslinking and gel-retarding system, the ligand L is different from the ligand L'.

CLAIMS

1. An aqueous gellable composition, containing an organic, water-soluble polymer crosslinkable with chrome ion and a crosslinking and gel-retarding system definable by the formula:

$$Cr(L)_m.nL'$$

L' being in form not complexed with chrome ion

wherein:

Cr is a trivalent chrome ion;

L is an organic ligand consisting of a monocarboxylate or dicarboxylate ion, optionally bearing one or more amino or hydroxy functional group(s), in form complexed with chrome ion;

L' is an organic ligand selected among malonic and ascorbic acids or when L' is salicylic acid, L is selected among: acetate, propionate, butyrate, malonate, succinate, glutarate, adipate, glycolate, lactate, alpha-hydroxybutyrate, ascorbate, tartrate, alpha-aminoacetate (glycine) and alpha-amino-beta-hydroxypropionate (serine), alpha-aminobutyrate, phthalate; in form complexed with chromium ion;

m has a value comprised within the range of from 1 to 3, depending on the nature of the ligand L;

n has a value comprised within the range of from 0.5 to 100;

with the proviso that in the crosslinking/retardant system, the ligand L is different from the ligand L'.

2. The composition according to claim 1, characterized in that in the crosslinking and gel-retarding system, the molar ratio of the ligand L' to chrome is comprised within the range of from 0.5:1 to 50:1.

3. The composition according to claim 1, characterized in that the concentration of chrome ion in the composition is comprised within the range of from 10 to 5,000 ppm.

4. The composition according to claim 3, characterized in that the concentration is comprised within the range of from 25 to 800 ppm.

5. The composition according to claims 3 and 4, characterized in that the concentration is comprised within the range of from 100 to 600 ppm.

6. The composition according to claim 1, characterized in that the concentration of the water-soluble organic polymer is comprised within the range of from 1,000 to 80,000 ppm, when salt water is used.

7. The composition according to claim 6, characterized in that the concentration is comprised within the range of 3,000 to 50,000 ppm when salt water is used.

8. The composition according to claim 6, characterized in that the concentration is comprised within the range of 5,000 to 10,000 ppm when salt water is used.

9. The composition according to claim 1, characterized in that said ligands L and L' of the

crosslinking and gel-retarding system are selected from among:

- monocarboxy aliphatic acids R-COOH, wherein R is a C_1-C_6 alkyl radical;
- dicarboxy aliphatic acids HOOC-$(CH_2)_a$-COOH, wherein a has a value comprised within the range of from 0 to 4, and relevant monoesters and monoamides;
- aliphatic alpha-hydroxyacids R'-CH(OH)-COOH, in which R' is a hydrogen atom, or an alkyl or hydroxyalkyl radical containing from 1 to 6 carbon atoms in its alkyl or hydroxyalkyl moiety, and the lactones thereof;
- aliphatic alpha-aminoacids R"-CH(NH_2)-COOH, wherein R" is a hydrogen atom, or an alkyl or hydroxyalkyl radical containing from 1 to 6 carbon atoms in its alkyl or hydroxyalkyl moiety;
- aromatic alpha-dicarboxy acids; and
- aromatic alpha-hydroxyacids.

10. The composition according to claim 9, characterized in that said ligands L and L' are: acetic acid, propionic acid and butyric acid; malonic acid, succinic acid, glutaric acid and adipic acid; glycolic acid, lactic acid, alpha-hydroxybutyric acid, ascorbic acid and tartaric acid; glycine, alpha-aminobutyric acid and serine; phthalic acid; and salicylic acid.

11. The composition according to claim 10, characterized in that the ligand L is acetate or malonate or glycolate ion and the ligand L' is selected from among: malonic acid, ascorbic acid, glycolic acid, alpha-

hydroxybutyric acid, alpha-aminobutyric acid, serine, phthalic acid and monoamide of glutaric acid.

12. The composition according to claim 11, characterized in that said crosslinking and gel-retarding system is selected from among:

- $Cr(acetate)_3$. n malonic acid,
  with n comprised within the range of from 0.5 to 100;
- $Cr(acetate)_3$. n salycilic acid,
  with n comprised within the range of from 0.5 to 50;
- $Cr(acetate)_3$. n ascorbic acid,
  with n comprised within the range of from 0.5 to 100;
- $Cr(malonate)_3$. n salycilic acid,
  with n comprised within the range of from 0.5 to 50; and
- $Cr(glycolate)_3$. n malonic acid,
  with n comprised within the range of from 0.5 to 100;
- $Cr(malonate)_3$.n glycolic acid,
  with n comprised within the range of from 0.5 to 100.

13. The composition according to claim 1, characterized in that the crosslinking and gel-retarding system additionally contains one or more hydroxy ions and/or neutral molecules and other monovalent and divalent inorganic ions, suitable for balancing the charge of the same system.

14. The composition according to claim 13, wherein the neutral molecules is water or pyridine.

15. The composition according to claim 13, wherein the monovalent inorganic ions are Na^+ and K^+.

16. The composition according to claim 1, characterized in that said organic polymer is selected from the group consisting of acrylamide homopolymers and acrylamide copolymers with one or more copolymerisable unsaturated monomer(s) selected from the group consisting of acrylic acid, methacrylamide, sodium 2-acrylamido-2-methyl-propane-sulfonate and N-vinyl-2-pyrrolidone, which acrylamide homopolymers or copolymers have a molecular weight comprised within the range of from 100,000 to 20,000,000, and preferably of from 200,000 to 12,000,000, said acrylamide homopolymers and copolymers being substantially non-hydrolysed (less than 1% of amidic groups hydrolysed into free carboxy groups), or partially hydrolysed (more than 1% of amidic groups hydrolysed into free carboxy groups).

17. The composition according to claim 15, characterized in that the copolymers of acrylamide with sodium 2-acrylamido-2-methyl-propane-sulfonate, the copolymers of acrylamide with N-vinyl-2-pyrrolidone and the terpolymers of acrylamide with sodium 2-acrylamido-2-methyl-propane-sulfonate and N-vinyl-2-pyrrolidone are used.

18. The composition according to claim 1, characterized in that it additionally contains one or more stabilizer agent(s) for the polymer.

19. The composition according to claim 17, wherein the stabilizer agent is thiourea.

20. The composition according to claim 1, characterized in that it has a pH value comprised within the range of from about 2 to about 9.

21. The composition according to claim 19, wherein the pH value is within the range of from about 4 to 7.

22. Process for reducing the permeability in a petroleum reservoir, which process comprises the following steps:

(a) preparing an aqueous gellable composition as claimed in claim 1;

(b) injecting said gellable composition into the petroleum reservoir through at least one well;

(c) causing said composition to flow through the reservoir, until it reaches and substantially fills the high-permeability region which has to be treated; and

(d) causing said composition to turn into a gel, with the permeability of the above said region being consequently decreased.

Fig.1

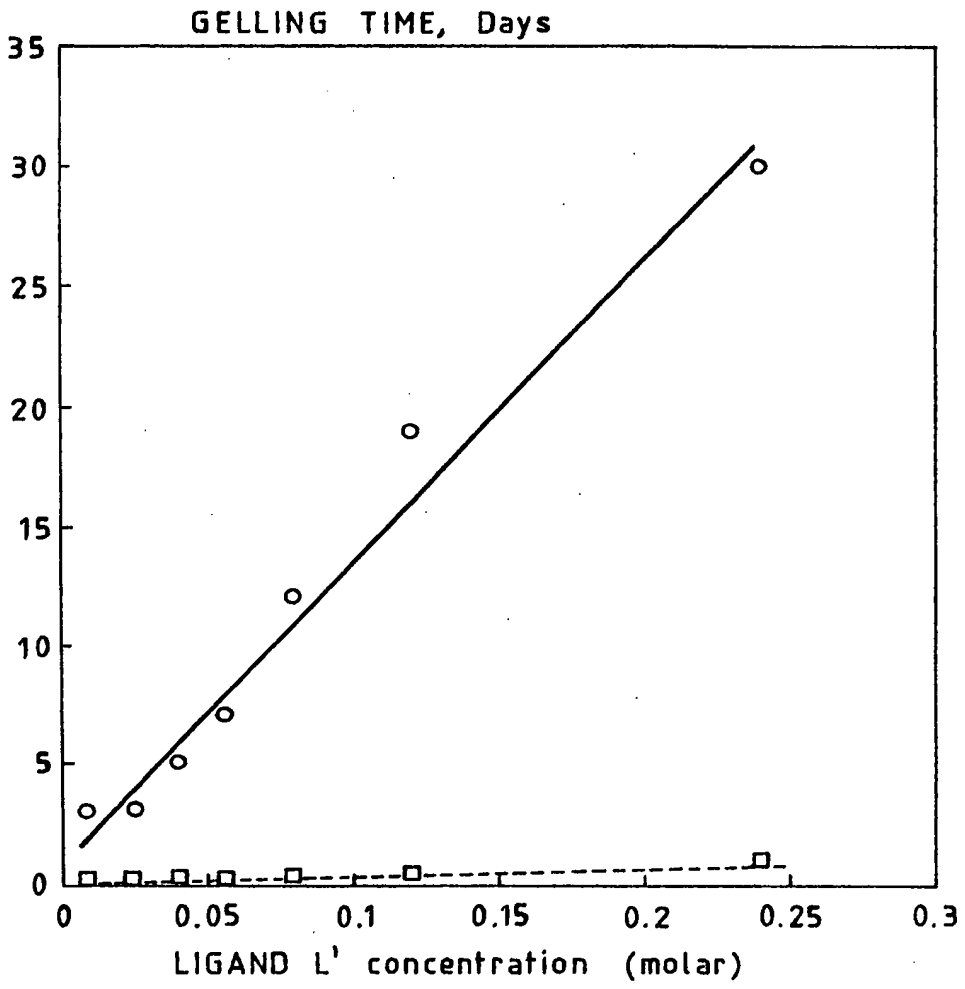

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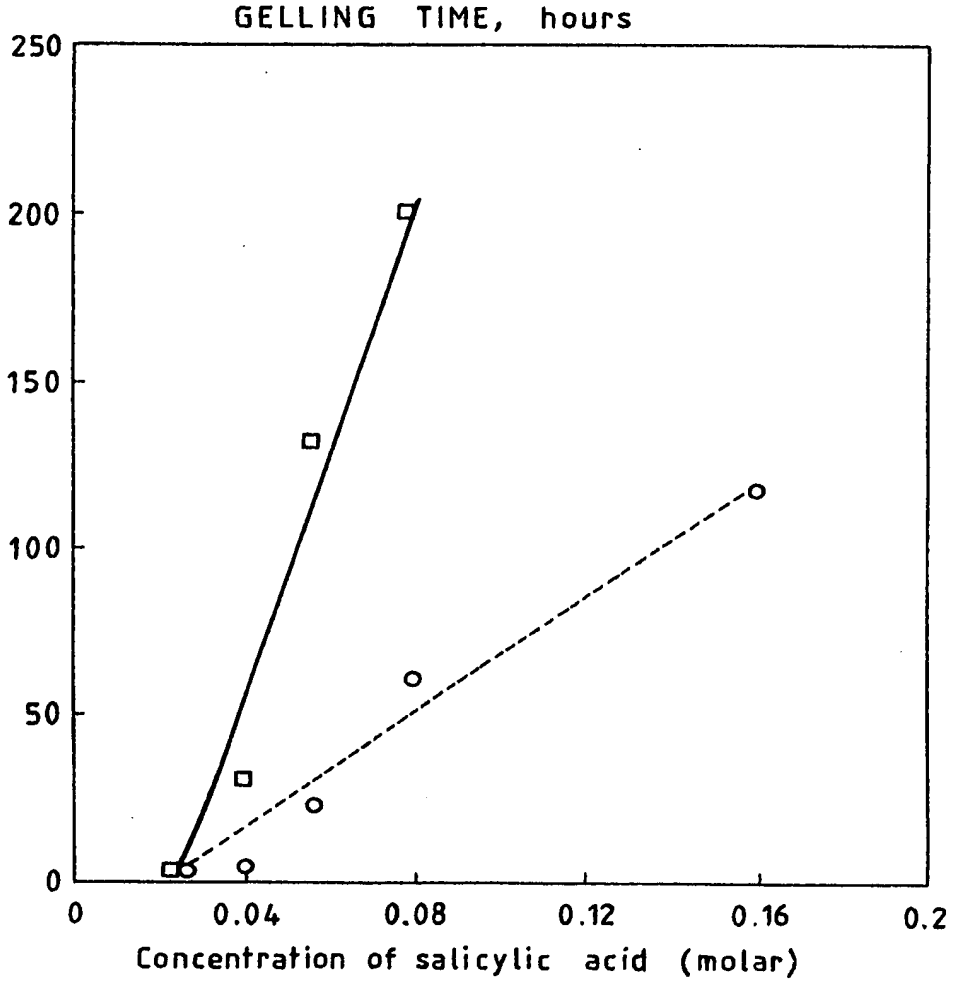
Fig.2



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